

# Casimir-Polder Forces between Chiral Objects

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**Abstract.** The chiral component of the Casimir-Polder potential is derived within the framework of macroscopic quantum electrodynamics. It is shown to exist only if the particle and the medium are both chiral. Furthermore, the chiral component of the Casimir-Polder potential can be attractive or repulsive, depending on the chirality of the molecule and the medium. The theory is applied to a cavity geometry in the non-retarded limit with the intention of enantiomer separation. For a ground state molecule the chiral component is dominated by the electric component and thus no explicit separation will happen. If the molecule is initially in an excited state the electric component of the Casimir-Polder force can be suppressed by an appropriate choice of material and the chiral component can select the molecule based on its chirality, allowing enantiomeric separation to occur.

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## 1. Introduction

A three-dimensional object that cannot be superimposed on its mirror image is said to be chiral, these distinct mirror images are called enantiomers. Spectroscopically, enantiomers have identical properties and distinguishing between the two is not trivial. The characteristic feature of chiral objects is the manner of their interactions with other chiral objects. For example, the refractive indices of left- and right-handed circularly polarised light are different in a chiral medium, therefore the two polarisations will propagate at different speeds. The difference in velocity is related to the phenomenon of circular dichroism, where the wave with the ‘slower’ polarisation is absorbed more strongly as it travels through the medium [1].

Many of the processes crucial to life involve chiral molecules whose chiral identity plays a central role in their chemical reactions, the incorrect enantiomer reacting differently and not producing the required result. In nature these molecules only occur as one enantiomer and are not found as the other, thus the reactions only occur when the correct enantiomer is present. In contrast, artificial production creates both enantiomers in equal proportions. Therefore it is important to be able to distinguish between enantiomers and ultimately to be able to separate a racemic (containing both enantiomers) mixture into an enantiomerically pure sample.

A frequently used method to separate enantiomers in an industrial setting is chiral chromatography. The initial racemic solution is passed through a column packed with a resolving agent, which is usually an enzyme and by necessity has to be chiral. This either retards, or stops, the progress of one of the enantiomers passing through the column but crucially not for the other and thus allows the solution to be separated. From an optical viewpoint it has been proposed that a racemic sample can be purified by use of coordinated laser pulses, which use a two-step process to initially drive

different transitions in the enantiomers before converting one into the other [2]. It has recently been calculated that in the presence of a chiral carbon nanotube the enantiomers of alanine possess different absorption energies and it was theorised that this could lead to a method of discrimination [3]. Furthermore, it has been shown that the van der Waals dispersion force between molecules can be enantiomer selective [4, 5]. Here we propose the use of another dispersion force, the Casimir-Polder force [6], as a method of distinguishing and ultimately separating enantiomers.

Casimir-Polder forces occur due to fluctuations in the quantum vacuum between objects, in this case it is between a particle and a macroscopic body. This force can be decomposed into an electric component that is solely dependent upon the electric dipole moments of the particle, the magnetic component of the force is likewise defined. We show that there is a third component that depends upon an interaction of the molecule's electric and magnetic dipole moments and this describes the particles chiral response in the chiral component of the Casimir-Polder force. For the purpose of discrimination, the force on enantiomers must be different, this means that a chiral medium is required to produce the chiral-selective behaviour.

Chiral molecules occur frequently in nature and there has been much work to calculate the relevant transition values either *ab initio* [7, 8], or through a twisted arc model for simple chiral molecules [9]. Recent technological developments have allowed for the creation of chiral fullerenes such as  $C_{76}$  [10], chiral carbon nanotubes [3] and chiral meta-materials [11]. Chiral meta-materials can be made from structures such as a gold helix [12], which shows a broadband electromagnetic response; a woodpile structure [13], a gold bar construction [14], which exhibit a negative refractive index in certain frequency ranges; and gold dots, [15] which can be tuned during construction to give a desired response. Recently it has been shown that superchiral electromagnetic fields [16] can arise in planar chiral metamaterials. These fields can generate a much larger dissymmetry between the effective refractive indices for adsorbed chiral molecules on left- and right-handed materials than circularly polarised light and a solution of chiral molecules [17]. Chiral metamaterials have also been proposed as a method of producing repulsive Casimir forces [18].

In this article we derive the chiral component of the Casimir-Polder potential within the framework of macroscopic quantum electrodynamics [19]. We show that inherent to this potential is the requirement that the particle and the medium both exhibit a chiral response. The theory is applied to the case of a chiral molecule in a cavity between two chiral metamaterials in the non-retarded limit, where we show a possible route towards enantiomer separation.

The article is organised as follows. The quantised description of a chiral medium is given in section 2.1, followed by the derivation of the chiral component of the Casimir-Polder force in section 2.2. This is applied to the case of a chiral molecule near a boundary; a perfect chiral mirror is considered in section 3.1 and a chiral metamaterial in section 3.2. We illustrate the theory by examining a chiral molecule in a cavity made of chiral metamaterials, considering a molecule initially in the ground state in section 4.1 and initially in an excited state in section 4.2. We provide some concluding remarks in section 5.

## 2. Formalism

In order to derive the chiral component of the Casimir-Polder potential in a general form, field quantisation in an absorbing chiral medium is required. This quantisation is

the basis for describing the electric and magnetic fields and the subsequent formulation of an important integral relation, which is needed for the calculation of the Casimir-Polder potential.

### 2.1. Chiral Media

The constitutive relations for the electromagnetic fields in the presence of a classical, non-dissipative chiral medium are given by

$$\mathbf{D} = \varepsilon_0 \boldsymbol{\varepsilon} \star \mathbf{E} - \frac{i}{c} \boldsymbol{\kappa}^T \star \mathbf{H} \quad (1)$$

and

$$\mathbf{B} = \frac{i}{c} \boldsymbol{\kappa} \star \mathbf{E} + \mu_0 \boldsymbol{\mu} \star \mathbf{H} \quad (2)$$

where  $\boldsymbol{\varepsilon}$  and  $\boldsymbol{\mu}$  are the relative permittivity and permeability tensors and  $\boldsymbol{\kappa}$  is the chirality tensor, a magnetoelectric susceptibility. The chiral susceptibility of the medium has the effect of ‘rotating’ a magnetic effect to contribute towards an electric response and vice versa. The  $\star$  is a notational shorthand for a spatial convolution, i.e.,  $[\mathbf{X} \star \mathbf{Y}](\mathbf{r}, \mathbf{r}') = \int d^3\mathbf{s} \mathbf{X}(\mathbf{r}, \mathbf{s}) \cdot \mathbf{Y}(\mathbf{s}, \mathbf{r}')$ . For nonlocally responding media the permittivity, permeability and chiral susceptibilities take the form  $\boldsymbol{\varepsilon}(\mathbf{r}, \mathbf{r}', \omega)$ , etc., where the two spatial variables are independent. This reduces to the form  $\boldsymbol{\varepsilon}(\mathbf{r}, \omega) \delta(\mathbf{r} - \mathbf{r}')$  in a locally responding medium. The medium is assumed to be reciprocal, i.e.  $\boldsymbol{\varepsilon}(\mathbf{r}, \mathbf{r}') = \boldsymbol{\varepsilon}^T(\mathbf{r}', \mathbf{r})$  and  $\boldsymbol{\mu}(\mathbf{r}, \mathbf{r}') = \boldsymbol{\mu}^T(\mathbf{r}', \mathbf{r})$ .

The Casimir-Polder force requires field quantisation in a medium due to its explicit quantum nature. In an absorbing medium, the quantum version of the constitutive relations are given as [20]

$$\hat{\mathbf{D}} = \varepsilon_0 \boldsymbol{\varepsilon} \star \hat{\mathbf{E}} - \frac{i}{c} \boldsymbol{\kappa}^T \star \hat{\mathbf{H}} + \hat{\mathbf{P}}_N - \frac{i}{c} \boldsymbol{\kappa}^T \star \hat{\mathbf{M}}_N \quad (3)$$

and

$$\hat{\mathbf{B}} = \frac{i}{c} \boldsymbol{\kappa} \star \hat{\mathbf{E}} + \mu_0 \boldsymbol{\mu} \star \hat{\mathbf{H}} + \mu_0 \boldsymbol{\mu} \star \hat{\mathbf{M}}_N. \quad (4)$$

The terms  $\hat{\mathbf{P}}_N$  and  $\hat{\mathbf{M}}_N$  are the noise polarisation and magnetisation respectively, they describe the dissipation in the medium and form a Langevin noise current

$$\hat{\mathbf{j}}_N(\mathbf{r}, \omega) = -i\omega \hat{\mathbf{P}}_N(\mathbf{r}, \omega) + \nabla \times \hat{\mathbf{M}}_N(\mathbf{r}, \omega). \quad (5)$$

The wave equation for the electric field in the chiral medium is then

$$\left[ \nabla \times \boldsymbol{\mu}^{-1} \star \nabla \times + \frac{\omega}{c} (\nabla \times \boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa} + \boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1} \star \nabla \times) - \frac{\omega^2}{c^2} (\boldsymbol{\varepsilon} - \boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa}) \right] \star \hat{\mathbf{E}} = i\omega \mu_0 \hat{\mathbf{j}}_N \quad (6)$$

and the Green’s tensor,  $\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)$ , is the fundamental solution to the above inhomogeneous Helmholtz equation

$$\left\{ \left[ \nabla \times \boldsymbol{\mu}^{-1} \star \nabla \times + \frac{\omega}{c} (\nabla \times \boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa} + \boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1} \star \nabla \times) - \frac{\omega^2}{c^2} (\boldsymbol{\varepsilon} - \boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa}) \right] \star \mathbf{G} \right\}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (7)$$

The Green’s tensor obeys the Schwarz reflection principle,

$$\mathbf{G}^*(\mathbf{r}, \mathbf{r}', \omega) = \mathbf{G}(\mathbf{r}, \mathbf{r}', -\omega^*), \quad (8)$$

which ensures reality of  $\mathbf{G}(\mathbf{r}, \mathbf{r}', t)$ , and inherits compliance with the Onsager condition for reciprocal media from the medium response functions

$$\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \mathbf{G}^T(\mathbf{r}', \mathbf{r}, \omega). \quad (9)$$

The wave equation and its Green's-tensor solution uniquely define the electric field (in coordinate space) as

$$\hat{\mathbf{E}}(\mathbf{r}, \omega) = i\omega\mu_0 \int d^3\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \cdot \hat{\mathbf{j}}_N(\mathbf{r}', \omega) \quad (10)$$

and the magnetic induction field as

$$\hat{\mathbf{B}}(\mathbf{r}, \omega) = \mu_0 \int d^3\mathbf{r}' \nabla \times \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \cdot \hat{\mathbf{j}}_N(\mathbf{r}', \omega). \quad (11)$$

To describe a general dissipative chiral medium, it is necessary to introduce the fundamental degrees of freedom of the field-medium system. Starting with the commutation relations for the noise polarisation and magnetisation [20]

$$\begin{aligned} & [\hat{\mathbf{P}}_N(\mathbf{r}, \omega), \hat{\mathbf{P}}_N^\dagger(\mathbf{r}', \omega')] \\ &= \frac{\varepsilon_0 \hbar}{\pi} \{ \text{Im}[\varepsilon(\omega) - \boldsymbol{\kappa}^T(\omega) \star \boldsymbol{\mu}^{-1}(\omega) \star \boldsymbol{\kappa}(\omega)] \}(\mathbf{r}, \mathbf{r}') \delta(\omega - \omega'), \end{aligned} \quad (12)$$

$$\begin{aligned} & [\hat{\mathbf{P}}_N(\mathbf{r}, \omega), \hat{\mathbf{M}}_N^\dagger(\mathbf{r}', \omega')] \\ &= \frac{\hbar}{iZ_0\pi} \{ \text{Im}[\boldsymbol{\kappa}^T(\omega) \star \boldsymbol{\mu}^{-1}(\omega)] \}(\mathbf{r}, \mathbf{r}') \delta(\omega - \omega'), \end{aligned} \quad (13)$$

$$\begin{aligned} & [\hat{\mathbf{M}}_N(\mathbf{r}, \omega), \hat{\mathbf{P}}_N^\dagger(\mathbf{r}', \omega')] \\ &= -\frac{\hbar}{iZ_0\pi} \{ \text{Im}[\boldsymbol{\mu}^{-1}(\omega) \star \boldsymbol{\kappa}(\omega)] \}(\mathbf{r}, \mathbf{r}') \delta(\omega - \omega'), \end{aligned} \quad (14)$$

$$[\hat{\mathbf{M}}_N(\mathbf{r}, \omega), \hat{\mathbf{M}}_N^\dagger(\mathbf{r}', \omega')] = -\frac{\hbar}{\mu_0\pi} \text{Im}[\boldsymbol{\mu}^{-1}(\mathbf{r}, \mathbf{r}', \omega)] \delta(\omega - \omega'), \quad (15)$$

the noise polarisation and magnetisation can be decomposed into

$$\begin{pmatrix} \hat{\mathbf{P}}_N \\ \hat{\mathbf{M}}_N \end{pmatrix} = \sqrt{\frac{\hbar}{\pi}} \mathcal{R} \star \begin{pmatrix} \hat{\mathbf{f}}_e \\ \hat{\mathbf{f}}_m \end{pmatrix} \quad (16)$$

where  $\mathcal{R}$  is the 'square root' of the 6x6 response tensor,

$$\mathcal{R} \star \mathcal{R}^\dagger = \begin{pmatrix} \varepsilon_0 \text{Im}[\varepsilon - \boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa}] & \frac{\text{Im}[\boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1}]}{iZ_0} \\ -\frac{\text{Im}[\boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa}]}{iZ_0} & -\frac{\text{Im}[\boldsymbol{\mu}^{-1}]}{\mu_0} \end{pmatrix}, \quad (17)$$

which describes the dissipative properties of the medium, where  $Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}}$ . For a passive, isotropic medium the response functions are restricted by  $(\text{Im}[\boldsymbol{\kappa}])^2 < \text{Im}[\varepsilon]\text{Im}[\boldsymbol{\mu}]$  [21]. The vector fields  $\hat{\mathbf{f}}_e(\mathbf{r}, \omega)$  and  $\hat{\mathbf{f}}_m(\mathbf{r}, \omega)$  are the bosonic annihilation operators for the matter-electromagnetic field system and with the creation operators they obey the commutation relation

$$[\hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega), \hat{\mathbf{f}}_{\lambda'}^\dagger(\mathbf{r}', \omega')] = \delta_{\lambda\lambda'} \delta(\mathbf{r} - \mathbf{r}') \delta(\omega - \omega') \quad (18)$$

with  $\lambda, \lambda' = e, m$ . By rewriting the electric and magnetic fields as

$$\hat{\mathbf{E}}(\mathbf{r}, \omega) = \sum_{\lambda=e,m} \int d^3\mathbf{r}' \mathbf{G}_\lambda(\mathbf{r}, \mathbf{r}', \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}', \omega), \quad (19)$$

$$\hat{\mathbf{B}}(\mathbf{r}, \omega) = \sum_{\lambda=e,m} \int d^3\mathbf{r}' \nabla \times \mathbf{G}_\lambda(\mathbf{r}, \mathbf{r}', \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}', \omega) \quad (20)$$

and making use of (16) and (17) it can be shown that

$$\begin{pmatrix} \mathbf{G}_e(\mathbf{r}, \mathbf{r}', \omega) \\ \mathbf{G}_m(\mathbf{r}, \mathbf{r}', \omega) \end{pmatrix} = -i\mu_0\omega \sqrt{\frac{\hbar}{\pi}} [\mathbf{G}(\omega) \star \begin{pmatrix} i\omega \\ \times \nabla \end{pmatrix} \cdot \mathcal{R}(\omega)](\mathbf{r}, \mathbf{r}') \quad (21)$$

where the operation  $\times \nabla$  refers to taking the derivatives of the second spatial variable and mathematically is described as  $[\mathbf{T} \times \nabla]_{ij}(\mathbf{r}, \mathbf{r}') = \epsilon_{jkl} \partial'_l T_{ik}(\mathbf{r}, \mathbf{r}')$ .

We can now derive the following integral relation,

$$\sum_{\lambda=e,m} \int d^3\mathbf{s} \mathbf{G}_\lambda(\mathbf{r}, \mathbf{s}, \omega) \cdot \mathbf{G}_\lambda^\dagger(\mathbf{r}', \mathbf{s}, \omega) = \frac{\hbar\mu_0\omega^2}{\pi} \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega), \quad (22)$$

see Appendix A.

## 2.2. Chiral Casimir-Polder Potential

To derive the Casimir-Polder potential we start with the interaction Hamiltonian in multipolar coupling and long wavelength approximation, describing the interaction of a molecule with the electric and magnetic fields [19]

$$\hat{H}_{AF} = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r}_A) - \hat{\mathbf{m}} \cdot \hat{\mathbf{B}}(\mathbf{r}_A), \quad (23)$$

where diamagnetic interactions have been neglected. Initially the particle can be either in its ground state or an excited state and the energy shift due to the atom-field interaction, (23), is given by

$$\Delta E = \sum_{I \neq N} \frac{\langle N | \hat{H}_{AF} | I \rangle \langle I | \hat{H}_{AF} | N \rangle}{E_N - E_I}. \quad (24)$$

When multiplying out the matrix elements it is important to note that the cross terms involving both electric and magnetic dipole interactions do not vanish and are in fact responsible for the chiral interaction, i.e.,  $\langle N | -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r}_A) | I \rangle \langle I | -\hat{\mathbf{m}} \cdot \hat{\mathbf{B}}(\mathbf{r}_A) | N \rangle$  and  $\langle N | -\hat{\mathbf{m}} \cdot \hat{\mathbf{B}}(\mathbf{r}_A) | I \rangle \langle I | -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r}_A) | N \rangle \neq 0$ .

The initial state is denoted by  $|N\rangle = |n\rangle|\{0\}\rangle$  and the intermediate states  $|I\rangle = |k\rangle\hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega)|\{0\}\rangle$  where  $|\{0\}\rangle$  denotes the ground state of the matter-field system (upon which the bosonic creation operators  $\hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega)$  act) and  $|n\rangle$  and  $|k\rangle$  represent the initial and intermediate energy levels of the particle. The summation in (24) contains sums over molecular transitions, the polarisation modes of the electromagnetic fields and integrals over all space and positive frequencies

$$\sum_{I \neq N} \rightarrow \sum_k \sum_{\lambda=e,m} \int d^3\mathbf{r} \mathcal{P} \int_0^\infty d\omega$$

( $\mathcal{P}$ : principal value). Using the definitions of the electric (19) and magnetic induction (20) fields it can be shown that

$$\langle N | -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r}_A) | I \rangle = -\mathbf{d}_{nk} \cdot \mathbf{G}_\lambda(\mathbf{r}_A, \mathbf{r}, \omega), \quad (25)$$

$$\langle N | -\hat{\mathbf{m}} \cdot \hat{\mathbf{B}}(\mathbf{r}_A) | I \rangle = -\frac{\mathbf{m}_{nk} \cdot \nabla \times \mathbf{G}_\lambda(\mathbf{r}_A, \mathbf{r}, \omega)}{i\omega}, \quad (26)$$

where the electric dipole transition matrix elements are  $\langle n | \hat{\mathbf{d}} | k \rangle = \mathbf{d}_{nk}$  and  $\langle n | \hat{\mathbf{m}} | k \rangle = \mathbf{m}_{nk}$  the corresponding magnetic dipole moment matrix elements.

The electric and magnetic components of the Casimir-Polder potential are well known and the result can be found in [19]. Here we focus on the terms containing a single curl operation and a dependency on the electric and magnetic transition matrix elements as it is these terms that give rise to the chiral component of the Casimir-Polder potential:

$$\begin{aligned} \Delta E_c = & \frac{\mu_0}{\pi} \sum_k \mathcal{P} \int_0^\infty \frac{i d\omega \omega}{\omega_{kn} + \omega} \left[ \mathbf{d}_{nk} \cdot \text{Im}[\mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega)] \times \overleftarrow{\nabla}' \cdot \mathbf{m}_{kn} \right. \\ & \left. + \mathbf{m}_{nk} \cdot \nabla \times \text{Im}[\mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega)] \cdot \mathbf{d}_{kn} \right], \end{aligned} \quad (27)$$

the transition frequencies are defined as  $\omega_{kn} = \omega_k - \omega_n$ . The Casimir-Polder potential is the position dependent part of the total energy shift,  $\Delta E = \Delta E_0 + U(\mathbf{r}_A)$ , and so its only contribution arises from the scattering part of the Green's function,  $\mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', \omega)$ .

The imaginary part of the Green's tensor is written as  $\text{Im}[\mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega)] = \frac{1}{2i} [\mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) - \mathbf{G}^*(\mathbf{r}_A, \mathbf{r}_A, \omega)]$ . When the molecule is not initially in the ground state care needs to be taken of the poles that occur for transitions to states of lower energy than the initial state. By using contour integration techniques the off-resonant part of the Casimir-Polder potential can be obtained in terms of an integral over imaginary frequencies, whereas the resonant part is due to the residue at the poles. The result is

$$\begin{aligned} \Delta E_c = & -\frac{\mu_0 \hbar}{2\pi} \int_0^\infty d\xi \xi \left( \text{tr}[\Gamma_{em}(i\xi) \cdot \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi) \times \overleftarrow{\nabla}'] \right. \\ & + \text{tr}[\Gamma_{me}(i\xi) \cdot \nabla \times \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)] \\ & + i\mu_0 \sum_k \Theta(\omega_{nk}) \omega_{nk} (\mathbf{d}_{nk} \cdot \text{Re}[\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk})] \times \nabla' \cdot \mathbf{m}_{kn} \\ & \left. + \mathbf{m}_{nk} \cdot \nabla \times \text{Re}[\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk})] \cdot \mathbf{d}_{kn} \right), \end{aligned} \quad (28)$$

where

$$\Gamma_{em}(i\xi) = \frac{1}{\hbar} \sum_k \left( \frac{\mathbf{m}_{kn} \otimes \mathbf{d}_{nk}}{\omega_{kn} + i\xi} - \frac{\mathbf{m}_{kn} \otimes \mathbf{d}_{nk}}{\omega_{kn} - i\xi} \right), \quad (29)$$

$$\Gamma_{me}(i\xi) = \frac{1}{\hbar} \sum_k \left( \frac{\mathbf{d}_{kn} \otimes \mathbf{m}_{nk}}{\omega_{kn} + i\xi} - \frac{\mathbf{d}_{kn} \otimes \mathbf{m}_{nk}}{\omega_{kn} - i\xi} \right) \quad (30)$$

are chiral susceptibility tensors and  $\Theta(\omega_{nk})$  is a step function which is zero if  $\omega_{nk} < 0$ , i.e. for a transition to a higher energy state. For an isotropic particle ( $\mathbf{d} \otimes \mathbf{m} = \frac{\mathbf{d}\mathbf{m}}{3}$ ), (29) and (30) both reduce to

$$\Gamma(i\xi) = -\frac{2}{3\hbar} \sum_k \frac{\xi R_{nk}}{(\omega_{kn})^2 + \xi^2}. \quad (31)$$

The term  $R_{nk}$  is the optical rotatory strength and is defined as

$$R_{nk} = \text{Im}(\mathbf{d}_{nk} \cdot \mathbf{m}_{kn}). \quad (32)$$

It describes the interaction between electric and magnetic dipole moments in a molecule and, crucially, left and right-handed enantiomers differ in the sign of  $R_{nk}$  for a particular transition.

To further simplify (28), it can be shown that

$$\text{tr}[\mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) \times \overleftarrow{\nabla}'] = -\text{tr}[\nabla \times \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega)] \quad (33)$$

where the Onsager reciprocity relation (9) has been used. For the real part of the Green's function an equivalent expression holds. We can now write the chiral component of the Casimir-Polder potential as

$$U_c(\mathbf{r}_A) = -\frac{\hbar\mu_0}{\pi} \int_0^\infty d\xi \xi \Gamma(i\xi) \text{tr}[\nabla \times \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)] \\ + \frac{2\mu_0}{3} \sum_k \Theta(\omega_{nk}) \omega_{nk} R_{nk} \text{tr}[\nabla \times \text{Re}[\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk})]] \quad (34)$$

The requirement that a chiral object is needed to be able to distinguish between the chiral states of another object is fulfilled. As (34) shows we must have a chiral medium and a chiral molecule. If either the medium ( $\text{tr}[\nabla \times \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)] = 0$ ), or the particle ( $R_{nk} = 0$ ) is achiral there will not be a chiral component to the Casimir-Polder potential. This can be thought of as a generalisation to the Curie dissymmetry principle (originally formulated for crystal symmetries) and one may say: The Casimir-Polder potential cannot distinguish between molecules of different handedness if the medium does not possess chiral properties itself.

For reference, the off-resonant electric and magnetic Casimir-Polder potentials [19] and their resonant parts are

$$U_e(\mathbf{r}_A) = \frac{\hbar\mu_0}{2\pi} \int_0^\infty d\xi \xi^2 \text{tr}[\boldsymbol{\alpha}(i\xi) \cdot \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)] \\ - \mu_0 \sum_k \Theta(\omega_{nk}) \omega_{nk}^2 \mathbf{d}_{nk} \cdot \text{Re}[\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk})] \cdot \mathbf{d}_{kn} \quad (35)$$

and

$$U_m(\mathbf{r}_A) = \frac{\hbar\mu_0}{2\pi} \int_0^\infty d\xi \text{tr}[\boldsymbol{\beta}(i\xi) \cdot \nabla \times \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi) \times \overleftarrow{\nabla}'] \\ + \mu_0 \sum_k \Theta(\omega_{nk}) \mathbf{m}_{nk} \cdot \nabla \times \text{Re}[\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk})] \times \nabla' \cdot \mathbf{m}_{kn} \quad (36)$$

where

$$\boldsymbol{\alpha}(i\xi) = \frac{1}{\hbar} \sum_k \left( \frac{\mathbf{d}_{kn} \otimes \mathbf{d}_{nk}}{\omega_{kn} + i\xi} + \frac{\mathbf{d}_{nk} \otimes \mathbf{d}_{kn}}{\omega_{kn} - i\xi} \right) \quad (37)$$

and

$$\boldsymbol{\beta}(i\xi) = \frac{1}{\hbar} \sum_k \left( \frac{\mathbf{m}_{kn} \otimes \mathbf{m}_{nk}}{\omega_{kn} + i\xi} + \frac{\mathbf{m}_{nk} \otimes \mathbf{m}_{kn}}{\omega_{kn} - i\xi} \right) \quad (38)$$

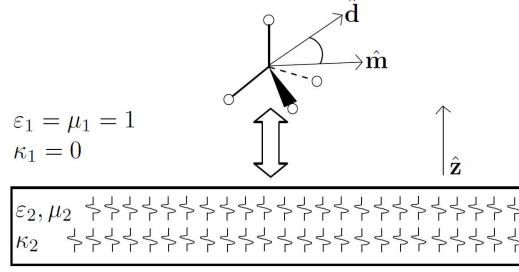
are the usual electric and magnetic susceptibilities.

### 3. Chiral Particle near a Chiral Halfspace

First we consider a chiral particle in free space near halfspace containing an isotropic chiral medium (figure 1). To compute the Casimir-Polder potential as given in (34) the scattering part of the Green's function for a source in free space near an isotropic chiral medium is required. The wave vectors travelling in the achiral region 1 are the standard free-space wave vectors

$$k_1^2 = \left(\frac{\omega}{c}\right)^2, \quad k_{1z}^2 = k_1^2 - k_{1q}^2 \quad (39)$$





**Figure 1.** Chiral molecule in free space near a chiral medium. The chiral molecule will have a different group or base (denoted by o) at the end of each bond, breaking the mirror symmetry. The boundary between the halfspaces is the  $(x, y)$  plane at  $z = 0$ . The isotropic chiral medium fills the space with  $z < 0$  (labelled region 2) and  $z > 0$  is the free-space (region 1).

where  $k_q^2 = k_x^2 + k_y^2$ . Within the chiral medium the wavevectors are

$$(k_2^R)^2 = \left(\frac{\omega}{c}\right)^2 (\kappa_2 + \sqrt{\varepsilon_2 \mu_2})^2, \quad (40)$$

$$(k_2^L)^2 = \left(\frac{\omega}{c}\right)^2 (-\kappa_2 + \sqrt{\varepsilon_2 \mu_2})^2, \quad (41)$$

$$(k_{2z}^P)^2 = (k_2^P)^2 - (k_{2q})^2, \quad (42)$$

where  $P = R, L$  and refers to the right and left circular polarisation of the wave, respectively.

The scattering part of the dyadic Green's function for a reflection from the achiral/chiral interface can be found in [22] as

$$\begin{aligned} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = & \frac{i}{8\pi^2} \frac{c}{\omega} \int d\mathbf{k}_{1\mathbf{q}} \frac{k_1}{k_{1z}} e^{i(\mathbf{k}_{1\mathbf{q}} \cdot (\mathbf{r}_{\mathbf{q}} - \mathbf{r}_{\mathbf{q}'}') + k_{1z}(z+z'))} \left[ \mathbf{e}_s \mathbf{e}_s R^{(s,s)} \right. \\ & \left. + \mathbf{e}_s \mathbf{e}_p (-k_{1z}) R^{(s,p)} + \mathbf{e}_p (k_{1z}) \mathbf{e}_s R^{(p,s)} + \mathbf{e}_p (k_{1z}) \mathbf{e}_p (-k_{1z}) R^{(p,p)} \right] \end{aligned} \quad (43)$$

where

$$\mathbf{e}_s = \frac{1}{k_q} (k_y \mathbf{x} - k_x \mathbf{y}) \quad (44)$$

and

$$\mathbf{e}_p(\pm k_z) = \frac{1}{k} (\mp k_z \mathbf{k}_q + k_q \mathbf{z}) \quad (45)$$

are the polarisation unit vectors for  $s$  and  $p$  polarised waves. The reflection coefficients  $R^{(s,s)}$ ,  $R^{(s,p)}$ ,  $R^{(p,s)}$  and  $R^{(p,p)}$  are typically dependent on the wave vectors given above and the medium response functions.

In this geometry the chiral component for the Casimir-Polder potential is

$$\begin{aligned} U_c(z_A) = & \frac{\hbar \mu_0}{4\pi^2 c} \int_0^\infty d\xi \xi^2 \Gamma(i\xi) \int_{\frac{\xi}{c}}^\infty d\tilde{k}_{1z} e^{-2\tilde{k}_{1z} z_A} \\ & \times \left[ \left( \frac{2\tilde{k}_{1z}^2 c^2}{\xi^2} - 1 \right) R^{(s,p)}(i\xi) + R^{(p,s)}(i\xi) \right] \end{aligned}$$

$$\begin{aligned}
& - \frac{\mu_0}{12\pi^2 c} \sum_k \Theta(\omega_{nk}) \omega_{nk}^2 R_{nk} \text{Re} \int d\mathbf{k}_{1q} \frac{e^{i2k_{1z}z_A}}{k_{1z}} \\
& \times \left[ \left( \frac{2k_{1z}^2 c^2}{\omega_{nk}^2} - 1 \right) R^{(s,p)}(\omega_{nk}) + R^{(p,s)}(\omega_{nk}) \right], \tag{46}
\end{aligned}$$

the details of this calculation can be found in Appendix B.

### 3.1. Perfect Chiral Mirror

As a purely theoretical construct we consider the potential between an isotropic molecule and an idealised medium that we have dubbed a ‘perfect chiral mirror’, whose reflection coefficients are  $R^{(s,p)}, R^{(p,s)} = \pm 1$  and therefore  $R^{(s,s)}, R^{(p,p)} = 0$ . This represents reflections where perpendicularly polarised waves are completely reflected into parallel polarised waves and vice versa. For a chiral medium that rotates the polarisation clockwise (with regard to the incoming wave - labelled ‘right-handed’) the reflection coefficients are  $R^{(s,p)} = 1$  and  $R^{(p,s)} = -1$  and for an anticlockwise polarisation rotation (labelled ‘left-handed’) they are  $R^{(s,p)} = -1$  and  $R^{(p,s)} = 1$ . When the molecule is initially in its ground state, applying these reflection coefficients to (46) results in

$$U(z_A) = \pm \frac{\hbar Z_0}{8\pi^2 z_A^3} \int_0^\infty d\xi \Gamma(i\xi) e^{-2\frac{\xi}{c}z_A} \left( \frac{2\xi z_A}{c} + 1 \right) \tag{47}$$

where the ‘+’ (upper sign) refers to the right-handed medium and ‘−’ (lower sign) refers to the left-handed medium. To examine how the spatial separation between the chiral particle and the chiral halfspace affects the chiral potential, we take the far-distance (retarded) and close-distance (non-retarded) limits of (47).

In the retarded limit where  $z_A \omega_{\min}/c \gg 1$  ( $\omega_{\min}$  is the minimum relevant particle transition frequency), the cross polarisability,  $\Gamma(i\xi)$ , approaches the static limit and can be approximated by  $\Gamma(i\xi) \approx \Gamma'(0)\xi$ . The potential becomes

$$U(z_A) = \mp \frac{Z_0 c^2}{16\pi^2 z_A^5} \sum_k \frac{R_{0k}}{(\omega_{k0})^2}. \tag{48}$$

In the non-retarded limit where  $z_A \omega_{\max}/c \ll 1$  ( $\omega_{\max}$  is the maximum relevant particle transition frequency) the potential becomes

$$U(z_A) = \pm \frac{Z_0}{12\pi^2 z_A^3} \sum_k R_{0k} \ln \left( \frac{\omega_{k0} z_A}{c} \right) \tag{49}$$

where use has been made of the relationship

$$\int_a^b dx \frac{x}{a^2 + x^2} \approx -\ln a, \text{ for } a \ll 1.$$

The results show a spatial scaling behaviour in the retarded and non-retarded limit that is different to the cases seen for dielectric or magnetic media in this geometry. An interesting consequence of such a medium is that in this simple geometry the electric and magnetic components of the Casimir-Polder potential would vanish. It should be noted that the potential can be attractive or repulsive depending on the medium and particle in question, in contrast to the purely attractive potentials that usually arise in this geometry. The chiral identity of both objects determines the character of the potential. The lack of electric and magnetic components of the Casimir-Polder potential and the existence of repulsive forces means that perfect chiral mirrors used in

a cavity or Fabry-Pérot geometry could be used to separate enantiomers. We believe that the results represent a theoretical upper bound for the chiral Casimir-Polder potential, however, they are physically unrealisable. This is because it would require a medium that completely rotates the polarisation of the incident waves and perfectly reflects the waves. Typically, the chirality of a medium will be restricted to  $\kappa^2 < \varepsilon\mu$ , which would exclude a perfect chiral mirror.

### 3.2. Isotropic Chiral Medium

For all realistic media, the reflection coefficients are not unity as there will always be transmission and losses from the fields as they are reflected. The reflection coefficients for an isotropic medium are given in [22], after taking the non-retarded limit they are

$$R^{(s,p)} = -R^{(p,s)} = \frac{2i\kappa_2}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1}, \quad (50)$$

$$R^{(s,s)} = \frac{\varepsilon_2\mu_2 - \kappa_2^2 - \varepsilon_2 + \mu_2 - 1}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1} \quad (51)$$

and

$$R^{(p,p)} = \frac{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 - \mu_2 - 1}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1}. \quad (52)$$

By setting  $\kappa_2 = 0$  the cross reflection coefficients disappear and  $R^{(s,s)}, R^{(p,p)}$  revert to the standard Fresnel reflection coefficients in the non-retarded limit.

We can now obtain the chiral-corrected electric component and the chiral component of the Casimir-Polder potential in the non-retarded limit. The off-resonant terms read

$$U_{eO}(z_A) = -\frac{\hbar}{16\pi^2\varepsilon_0 z_A^3} \int_0^\infty d\xi \alpha(i\xi) \times \left[ \frac{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 - \mu_2 - 1}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1} \right], \quad (53)$$

$$U_{cO}(z_A) = \frac{\hbar Z_0}{4\pi^2 z_A^3} \int_0^\infty d\xi \Gamma(i\xi) \left[ \frac{i\kappa_2}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1} \right], \quad (54)$$

where all response functions are dependent on complex frequency, i.e.,  $\varepsilon_2 = \varepsilon_2(i\xi)$ ,  $\mu_2 = \mu_2(i\xi)$  and  $\kappa_2 = \kappa_2(i\xi)$ . The resonant terms are

$$U_{eR}(z_A) = -\frac{1}{24\pi\varepsilon_0 z_A^3} \sum_k \Theta(\omega_{nk}) |d_{nk}|^2 \times \text{Re} \left[ \frac{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 - \mu_2 - 1}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1} \right], \quad (55)$$

$$U_{cR}(z_A) = \frac{Z_0}{6\pi z_A^3} \sum_k \Theta(\omega_{nk}) R_{nk} \times \text{Im} \left[ \frac{i\kappa_2}{\varepsilon_2\mu_2 - \kappa_2^2 + \varepsilon_2 + \mu_2 + 1} \right], \quad (56)$$

where the response functions in (55) and (56) are taken at the transition frequency,  $\omega_{nk}$  i.e.,  $\varepsilon_2 = \varepsilon_2(\omega_{nk})$ ,  $\mu_2 = \mu_2(\omega_{nk})$  and  $\kappa_2 = \kappa_2(\omega_{nk})$ . As a consistency check, setting  $\mu_2 = 1$  and letting  $\kappa_2 \rightarrow 0$  in the off-resonant contribution the results for the electric component of the Casimir-Polder potential between a particle and a dielectric in [19] are recovered.

#### 4. Chiral Cavity

To examine whether the Casimir-Polder force can be used to distinguish between enantiomers, we consider a chiral molecule in free space between two chiral media which differ only in their handedness. To illustrate this we have selected a chiral metamaterial whose parameters have been published in [13] as the chiral medium due to the strong chirality that can be obtained from metamaterials. To characterise the medium a single-resonance Drude-Lorentz model is used for  $\varepsilon(\omega)$  and  $\mu(\omega)$  and the Condon model [1, 23] is used for  $\kappa(\omega)$ . These are

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - \omega_E^2 + i\gamma_E\omega}, \quad (57)$$

$$\mu(\omega) = 1 - \frac{\omega_m^2}{\omega^2 - \omega_B^2 + i\gamma_B\omega} \quad (58)$$

and

$$\kappa(\omega) = \frac{a\omega}{\omega^2 - \omega_C^2 + i\gamma_C\omega}. \quad (59)$$

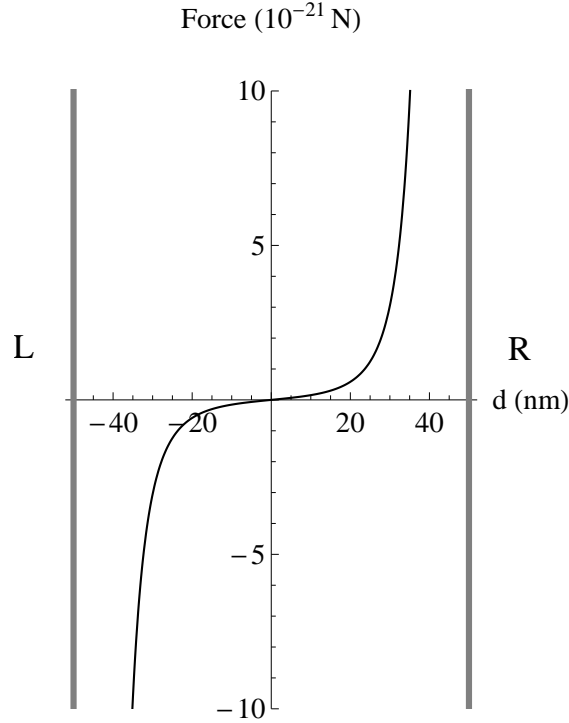
The constants  $\omega_p, \omega_m$  and  $a$  represent the oscillator strengths for the dipole transitions responsible for  $\varepsilon$ ,  $\mu$  and the rotatory strength associated with  $\kappa$ , respectively. The remaining constants are the resonant frequencies and damping factors for the permittivity ( $\omega_E, \gamma_E$ ), permeability ( $\omega_B, \gamma_B$ ) and the chirality ( $\omega_C, \gamma_C$ ) of the medium.

For the chiral molecule, dimethyl disulphide  $(\text{CH}_3)_2\text{S}_2$  has been chosen. The dipole and rotatory strengths for each transition have been numerically calculated for various orientations [7]. As an example, we have chosen the first transition when the orientation between the two  $\text{CH}_3 - \text{S} - \text{S}$  planes is  $90^\circ$ . The transition frequency is  $\omega_{nk} = 9.17 \times 10^{15} \text{ s}^{-1}$ , dipole strength  $|\mathbf{d}_{nk}|^2 = 8.264 \times 10^{-60} (\text{C m})^2$  and the rotatory strength is  $R_{nk} = 3.328 \times 10^{-64} \text{ C}^2 \text{ m}^3 \text{ s}^{-1}$ .

##### 4.1. Ground-State Force

In the non-retarded limit, multiple reflections between the halfspaces are not considered and the forces on the molecule for each halfspace are simply added. From the Casimir-Polder potentials for the electric (53) and chiral (54) components we can obtain the forces ( $\mathbf{F} = -\nabla U$ ) acting on the molecule. The two halfspaces are identical except for their chirality, characterised by  $a$ , which is negative for one of the halfspaces and positive for the other. We assume that the molecule has only two energy levels, i.e. only one transition is considered.

By considering a separation between the halfspaces of 100nm we obtain the results shown in figure 2 and figure 3. The electric component of the Casimir-Polder force (figure 2) is always attractive towards both halfspaces. In this geometry these forces are equal and opposite, so when computing the electric component of the total force (in the non-retarded limit) on the molecule, the halfspace closest to the molecule will provide the dominant contribution to this total force. By implication, when the molecule is in the centre (i.e. equal distance from both halfspaces), the electric components of the Casimir-Polder force cancel and the net contribution to the total Casimir-Polder force is zero. It should be noted that the difference in the chirality of the halfspaces does not effect the electric force from either halfspace and hence the combined electric component of the total force.

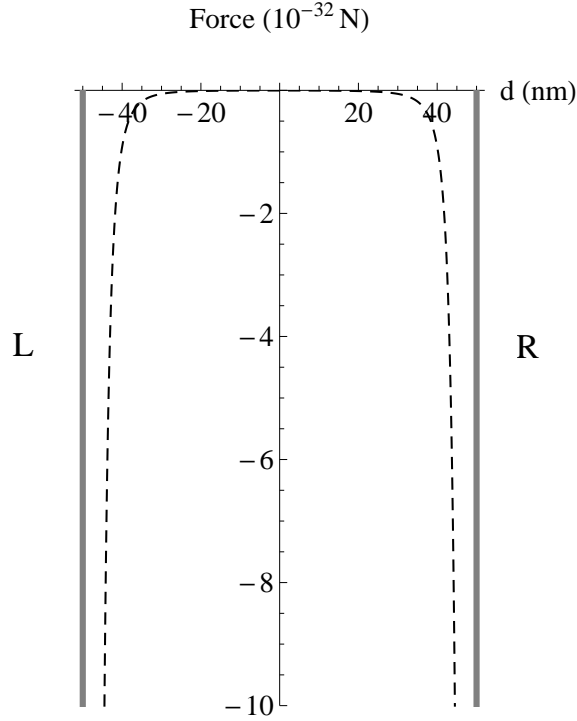


**Figure 2.** The electric component of the Casimir-Polder force. The molecule is attracted to both halfspaces with the stronger attraction coming from the closest halfspace. The vertical lines denote the boundaries of the metamaterial, the gap between is freespace where the molecule is located. The parameters obtained from [13] are  $\omega_p = 5.47 \times 10^{14} \text{ s}^{-1}$ ,  $\omega_m = 3.06 \times 10^{14} \text{ s}^{-1}$ ,  $a = -3.61 \times 10^{14} \text{ s}^{-1}$ ,  $\omega_E = \omega_B = \omega_C = 4.96 \times 10^{14} \text{ s}^{-1}$ ,  $\gamma_E = \gamma_B = 2.51 \times 10^{13} \text{ s}^{-1}$  and  $\gamma_C = -2.58 \times 10^{13} \text{ s}^{-1}$ .

By looking at the chiral component of the Casimir-Polder force (figure 3) one obtains an attractive force between the chiral molecule and one of the halfspaces (to the left hand side) and a repulsive force between the chiral molecule and the other halfspace (to the right hand side). Furthermore, the total chiral component of the force does not disappear at the midpoint between the halfspaces.

Figure 2 and figure 3 show that the electric component of the Casimir-Polder force is many orders of magnitude larger than the chiral component and will dominate interactions. The exception to this is the central region between the halfspaces, where the overall electric component is reduced sufficiently to allow the chiral component to become the dominant force. However, the width of this central region is smaller than the molecule. This means that for a particle initially in the ground state the Casimir-Polder force, in the current geometry, would not be able to distinguish between enantiomers and subsequently separate them.

The difference in orders of magnitude of the force components can be traced to separate origins. With regard to the chiral molecule the optical rotatory strength is orders of magnitude smaller than the electric dipole transition matrix element,  $R_{nk}/c \lesssim 10^{-11} |\mathbf{d}_{nk}|^2$ . This can be understood by the fact that the magnetic dipole moment appears at a higher-order of the multipole expansion than the electric



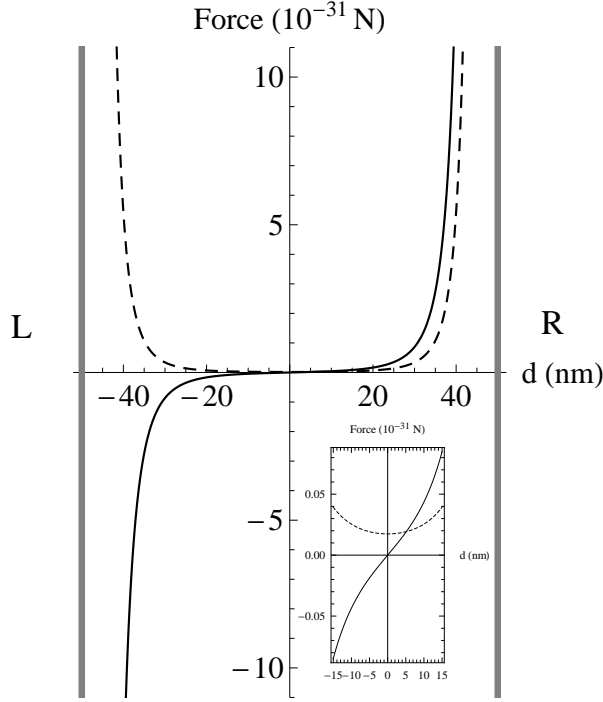
**Figure 3.** The chiral component of the Casimir-Polder force. The molecule is attracted to the left hand side halfspace and there is a repulsive force between the molecule and the right hand side halfspace.

dipole moment. Looking at the chiral medium, the chirality is slightly smaller than the permittivity, but this difference is enhanced by the structure of the reflection coefficients.

#### 4.2. Excited-State Force

In order to overcome the dominance of the electric dipole force, it is helpful to consider other molecular initial states. If the molecule is initially in an excited state the resonant contribution to the force needs to be considered. In this scenario, the off-resonant part of the electric component of the Casimir-Polder force is repulsive whereas the direction of the chiral off-resonant component is dependent on the chiral identity of the molecule and material in question. A metamaterial can be constructed such that for a given transition frequency the resonant contribution to the electric component of the Casimir-Polder force will counteract the off-resonant contribution. By creating a cavity with two such metamaterials, identical except for their chirality, a chiral molecule initially in an excited state can be separated from its enantiomer. This is because the suppression of the electric component of the Casimir-Polder force allows the chiral component of the force to attract an enantiomer to the corresponding halfspace while it is being repelled from the opposite halfspace without the electric component dominating.

As a proof of principle the metamaterials parameters are chosen as suitable



**Figure 4.** The total electric component of the Casimir-Polder force (black line) and the total chiral component (dashed line). The components of the force are of equal magnitude, with the chiral contribution larger in the centre and the electric contribution larger towards the halfspaces. The parameters are chosen as  $\omega_E = \omega_B = \omega_C = \frac{\omega_p}{2}$ ,  $\gamma_E = \gamma_B = -\gamma_C = \frac{\omega_p}{10^3}$ ,  $a = -\frac{\omega_p}{3}$  and  $\omega_m = \frac{\omega_p}{5}$ . The inset in the bottom right shows a magnification of the centre region between  $-15$  nm and  $15$  nm.

multiples of the plasma frequency and the values for the optical rotatory strength and dipole strength are as given above and the metamaterials are separated by 100 nm of free space.

The results are shown in figure 4. As can be seen, for a particular transition frequency a suppression of the electric component of the Casimir-Polder force sufficient to allow enantiomer separation can be obtained. The chiral component is the dominant contribution in the central region ( $\approx 10$  nm) of the cavity (see the inset to figure 4), meaning that the direction of the force acting on a chiral molecule in this region will be dependent on its chirality. Therefore enantiomers that pass at low speeds through the centre of the cavity will be attracted or repelled in opposite directions and will be separated based on their chirality. As the total electric component of the Casimir-Polder force is attractive, the separated enantiomers will continue to be drawn towards opposite halfspaces even when not in the central region.

It is important to note that, although the chirality of the metamaterials has not changed, the chiral component of the Casimir-Polder force is now acting in the opposite direction. This is due to the resonant part of the chiral force, which is larger than the off-resonant part and acts against it.

## 5. Conclusion

The chiral component of the Casimir-Polder potential has been derived within the framework of macroscopic QED. The results show that the medium and particle in question must both be chiral, otherwise this potential does not exist. Furthermore, this potential is sensitive to the chirality of the objects in question and can be attractive or repulsive.

By initially considering a perfect chiral mirror, it was found that in the retarded limit the chiral component of the Casimir-Polder potential scales as  $1/(z_A)^5$  with the molecule-surface distance whereas for the non-retarded limit the spatial scaling is  $1/(z_A)^3 \ln(z_A)$ . As already alluded to, it is unlikely that this could be realised in a real material, due to the requirement for perfect reflection *and* complete rotation of the incident wave polarisation. When the chiral medium does not exhibit perfect reflectance the chiral potential is slightly diminished and in the non-retarded limit the spatial scaling was found to be  $1/(z_A)^3$ .

In the geometry where a chiral molecule, initially in the ground state, is located between two half spaces of opposite chirality it was found that the chiral component of the Casimir-Polder force is attractive towards one half space and repulsive from the other. However, the electric component of the Casimir-Polder force between the molecule and the half spaces dominates over the chiral component. Therefore, in this geometry, it would not be possible to distinguish between enantiomers because the indiscriminate attractive electric force dominates over any chiral effects.

If the molecule is initially in an excited state it was found that the material properties can be tuned such that the resonant contribution to the electric component of the Casimir-Polder force almost completely suppresses the off-resonant contribution. Enantiomers in the centre between the halfspaces would then experience an overall force whose direction is dependent on the chiral identity of the molecule. This chiral force will draw the molecule towards a particular halfspace with its enantiomer attracted to the other side of the cavity. This distinction between enantiomers will allow them to be separated by the Casimir-Polder force.

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## References

- [1] E. U. Condon, *Rev. Mod. Phys.* **9**, 432 (1937).
- [2] P. Král, I. Thanopoulos, M. Shapiro and D. Cohen, *Phys. Rev. Lett.* **90**, 033001 (2003).
- [3] D. Vardanega, F. Picaud and C. Giradet, *Surface Science* **601**, 3818 (2007).
- [4] J. Trost and K. Hornberger, *Phys. Rev. Lett.* **103**, 023202 (2009).
- [5] D.P. Craig and T. Thirunamachandran, "Molecular Quantum Electrodynamics", *Academic Press* (1984).
- [6] H.B.G Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948).
- [7] A. Rauk, *J. Am. Chem. Soc.* **106**, 6517 (1984).
- [8] T. D. Crawford, *Theor Chem Acc* **115**, 227 (2006).
- [9] J. Trost and K. Hornberger, *Chem. Phys.* **335**, 115 (2007).
- [10] R. Ettl, I. Chao, F. Diederich and R.L. Whetten, *Nature* **353**, 149 (1991).
- [11] C.M. Soukoulis and M. Wegener, *Nature Photonics* **5**, 523 (2011).



- [12] J.K. Gansel, M. Thiel, M.S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden and M. Wegener, *Science* **325**, 1513 (2009).
- [13] M. S. Rill, C. E. Kriegler, M. Thiel, G. von Freymann, S. Linden and M. Wegener, *Optics Letters* **34**, 16 (2009).
- [14] S. Zhang, Y-S. Park, J. Li, X. Lu, W. Zhang and X. Zhang, *Phys. Rev. Lett.* **102**, 023901 (2009).
- [15] M. Hentschel, M. Schäferling, T. Weiss, N. Liu and H. Giessen, *NanoLett.* **12**, 2542 (2012).
- [16] Y. Tang and A.E. Cohen, *Phys. Rev. Lett.* **104**, 163901 (2010).
- [17] E. Hendry, T. Carpy, J. Johnston, M. Popland, R.V. Mikhaylovskiy, A.J. Lapthorn, S.M. Kelly, L.D. Barron, N. Gadegaard and M. Kadodwala, *Nature Nanotechnology* **5**, 783 (2010).
- [18] R. Zhao, J. Zhou, T. Koschny, E.N. Economou, and C.M. Soukoulis, *Phys. Rev. Lett.* **103**, 103602 (2009).
- [19] S. Scheel and S. Y. Buhmann, *Acta Physica Slovaca* **58**, 675 (2008).
- [20] S. Y. Buhmann, D. T. Butcher and S. Scheel, *New J. Phys.* **14**, 083034 (2012).
- [21] F. Guérin, *PIER* **9**, 31 (1994).
- [22] S. M. Ali, T. M. Habashy and J. A. Kong, *J. Opt. Soc. Am. A* **9**, 413 (1992).
- [23] N. L. Tsitsas, A. Lakhtakia and D. J. Frantzeskakis, *J. Phys. A: Math. Theor.* **44**, 435203 (2011).
- [24] H. C. Chen, "Theory of electromagnetic waves: a coordinate-free approach", *McGraw-Hill* (1983).

## Appendix A.

### Integral Relation

We begin by evaluating the left hand side of the integral equation (22). By taking the product of (21) with its hermitian conjugate we arrive at the term

$$\begin{aligned} \mathbf{G}_e \star \mathbf{G}_e^\dagger + \mathbf{G}_m \star \mathbf{G}_m^\dagger = \\ (\mu_0 \omega)^2 \frac{\hbar}{\pi} \mathbf{G} \star \left( \frac{i\omega}{\times \overleftarrow{\nabla}'} \right) \cdot \mathcal{R} \star \mathcal{R}^\dagger \cdot \left( \frac{i\omega}{\times \overleftarrow{\nabla}'} \right)^\dagger \star \mathbf{G}^\dagger. \end{aligned} \quad (\text{A.1})$$

Substituting in (17) leads to

$$\begin{aligned} \sum_{\lambda=e,m} \mathbf{G}_\lambda \star \mathbf{G}_\lambda^\dagger &= \frac{\hbar \mu_0 \omega^2}{\pi} \left[ \mathbf{G} \star \left[ \frac{\omega^2}{c^2} \text{Im}[\boldsymbol{\varepsilon} - \boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa}] \right. \right. \\ &+ \frac{\omega}{c} (\times \overleftarrow{\nabla}' \cdot \text{Im}[\boldsymbol{\mu}^{-1} \star \boldsymbol{\kappa}] - \text{Im}[\boldsymbol{\kappa}^T \star \boldsymbol{\mu}^{-1}] \cdot \nabla \times) \\ &\left. \left. + \times \overleftarrow{\nabla}' \cdot \text{Im}[\boldsymbol{\mu}^{-1}] \cdot \nabla \times \right] \star \mathbf{G}^\dagger \right]. \end{aligned} \quad (\text{A.2})$$

By comparing (A.2) with the noise polarisation and magnetisation commutators (12), (13), (14) and (15) it can be seen that this reduces to

$$\sum_{\lambda=e,m} \mathbf{G}_\lambda(\omega) \star \mathbf{G}_\lambda^\dagger(\omega) = \frac{\hbar \mu_0 \omega^2}{\pi} \left[ \mathbf{G}(\omega) \star [\hat{\mathbf{j}}_N(\omega), \hat{\mathbf{j}}_N^\dagger(\omega)] \star \mathbf{G}^\dagger(\omega) \right]. \quad (\text{A.3})$$

It is known that [20]

$$[\hat{\mathbf{j}}_N(\mathbf{r}, \omega), \hat{\mathbf{j}}_N^\dagger(\mathbf{r}', \omega')] = \frac{\hbar \omega}{\pi} \text{Re}[\mathbf{Q}(\mathbf{r}, \mathbf{r}', \omega)] \delta(\omega - \omega') \quad (\text{A.4})$$

where  $\mathbf{Q}$  is a complex conductivity tensor. This leads to the general form of the integral relation [20]

$$\begin{aligned} &\left( \frac{\hbar \mu_0 \omega^2}{\pi} \right) \mu_0 \omega [\mathbf{G}(\omega) \star \text{Re} \mathbf{Q}(\omega) \star \mathbf{G}^\dagger(\omega)](\mathbf{r}, \mathbf{r}') \\ &= \frac{\hbar \mu_0 \omega^2}{\pi} \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega). \end{aligned} \quad (\text{A.5})$$

Therefore,

$$\sum_{\lambda} [G_{\lambda}(\omega) \star G_{\lambda}^{\dagger}(\omega)](\mathbf{r}, \mathbf{r}') = \frac{\hbar \mu_0 \omega^2}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}', \omega), \quad (\text{A.6})$$

which in coordinate space is

$$\sum_{\lambda} \int d^3 \mathbf{s} G_{\lambda}(\mathbf{r}, \mathbf{s}, \omega) \cdot G_{\lambda}^{\dagger}(\mathbf{r}', \mathbf{s}, \omega) = \frac{\hbar \mu_0 \omega^2}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}', \omega), \quad (\text{A.7})$$

as required.

## Appendix B.

### Dyadic Green's Function Calculation

To obtain the chiral component of the Casimir-Polder force we require the terms for  $\text{tr}[\nabla \times \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, i\xi)]$  and  $\text{tr}[\nabla \times \text{Re}[\mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk})]]$ . It is known from dyadic algebra that [24]

$$\mathbf{u} \times \mathbf{a} \mathbf{b} = (\mathbf{u} \times \mathbf{a}) \mathbf{b} \quad (\text{B.1})$$

where  $\mathbf{a} \mathbf{b}$  is a dyadic product and subsequently  $(\mathbf{u} \times \mathbf{a}) \mathbf{b}$  is also a dyadic product. Applying (B.1) to (43) gives the effective results

$$\nabla \times \mathbf{e}_s = -ik \mathbf{e}_p(k_z), \quad (\text{B.2})$$

$$\nabla \times \mathbf{e}_p(k_z) = ik \mathbf{e}_s, \quad (\text{B.3})$$

where  $\nabla \rightarrow (ik_x, ik_y, ik_z)$ . Taking the trace of the dyadic Green's function is equivalent to taking the dot product between the dyads,

$$\mathbf{e}_s \cdot \mathbf{e}_p(-k_z) = \mathbf{e}_p(k_z) \cdot \mathbf{e}_s = 0, \quad (\text{B.4})$$

$$\mathbf{e}_s \cdot \mathbf{e}_s = 1, \quad \mathbf{e}_p(k_z) \cdot \mathbf{e}_p(-k_z) = 1 - \frac{2k_z^2}{k^2}. \quad (\text{B.5})$$

To calculate the off-resonant contribution the integration variable is changed to

$$\int d\mathbf{k}_q \rightarrow \int_0^{2\pi} d\theta \int_0^{\infty} dk_q k_q \rightarrow -2\pi \int_{\frac{\omega}{c}}^{\infty} dk_z k_z,$$

the wavevectors in complex frequency ( $\omega \rightarrow i\xi$ ) become

$$k_1 = i \frac{\xi}{c} = i \tilde{k}_1, k_{1z} = i \tilde{k}_{1z} \quad (\text{B.6})$$

with

$$\tilde{k}_{1z} = \sqrt{\left(\frac{\xi}{c}\right)^2 + (k_{1q})^2} \quad (\text{B.7})$$

in the achiral halfspace and

$$\begin{aligned} k_2^R &= i \left(\frac{\xi}{c}\right) (\kappa_2 + \sqrt{\varepsilon_2 \mu_2}) = i \tilde{k}_2^R, \\ k_2^L &= i \left(\frac{\xi}{c}\right) (-\kappa_2 + \sqrt{\varepsilon_2 \mu_2}) = i \tilde{k}_2^L, \\ k_{2z}^P &= i \tilde{k}_{2z}^P, \\ \tilde{k}_{2z}^P &= \sqrt{\left(\tilde{k}_2^P\right)^2 + (k_{2q})^2} \end{aligned} \quad (\text{B.8})$$

in the chiral halfspace.